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Characterizing the role of pesticides impacting surface water ecosystems in multiple stressed environments

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1. Introduction

Groundwater and surface water resources are increasingly under pressure from global exploitation and anthropogenic impacts, such as contamination by chemicals. In response, the European Water Framework Directive requires member states to evaluate all types of contamination sources within a watershed in order to assess their direct impact on water quality[1-3]. The clear linkage between these two systems requires assessments of "good" chemical and ecological status to include an evaluation of the contribution of toxicants entering surface water via the groundwater pathway.

Pesticides are among the most harmful class of compounds impacting surface waters, particularly since they have been so widely used to control the occurrence of pests and weeds in urban and agricultural landscapes[4]. In order to properly identify and subsequently mitigate the impacts to surface water ecosystems, a better understanding of the sources and types of pesticides expected in surface waters becomes essential. Here we (i) assess current trends for pesticide concentrations in surface water and compare them to the historical use of pesticides in Denmark (using sales data), (ii) investigate the importance of groundwater as a pathway for pesticide impacts to ecosystems, and (iii) quantify the impact of sediment-bound pesticides affecting stream macroinvertebrates. Notably, sediment-bound pesticides have long been disregarded as an important source of ecotoxicity, due predominantly to an assumed reduction in bioavailability.

2. Materials and methods

2.1. Study catchments and choice of pesticides

Fourteen headwater streams in four catchments located on Sjaelland, Denmark were selected, and the concentrations of pesticides – including select metabolites and impurities – were determined for the dissolved and sediment-bound phases. Two catchments were chosen where agriculture represents ≥80% of the land use; although these catchments differ in size (and thus number of tributaries) and degree of physical in-stream (habitat) degradation, they are similar in that the dominant arable crop types are wheat, barley and canola (visual observations 2010-2012). Two catchments were selected as least disturbed controls.

The chemicals in the study were selected to represent the most relevant pesticides with respect to past (banned herbicides commonly found in groundwater) and current-use (commonly applied), different physico-chemical properties and toxicity. We included a range of pesticides determined by evaluating the probable relationships between pesticide, crops and spraying practice, and sale statistics expected to be used in the catchments during 2010-2012[4].

2.2. Sampling campaign and toxicity calculation

The following pathways for pesticides in headwater streams were investigated: chronic exposure due to groundwater inflow, acute exposure due to storm-water runoff, and the presence of sediment-bound pesticides in streams. Sampling was conducted during May-August from 2010-2012. Aqueous-phase pesticides were sampled with event-triggered water samplers[5] during May and June to capture surface runoff and flow through tile drains during heavy precipitation events. Groundwater inflow of pesticides was grab-sampled in August, after a period with little to no precipitation. Sediment-bound phases were collected using two methods: suspended sediment floating with the stream water was collected using passive suspended particle samplers (SPS) placed in 4 selected streams during May-June for capturing the most lipophilic pesticides[6]. Additionally, streambed sediment was collected manually at 1 site in August using Kayak corers[7].

Pesticide analyses, including impacts to macroinvertebrates – calculated using the toxic units (TU) approach – are presented for twelve sampling locations in two watersheds in Denmark. The sum of all TUs (sumTU) is used instead of the maximum TU, in order to produce a conservative estimate for the toxicity, in line with the principle of screening-level risk assessments. Biomonitoring was conducted using the traditional Danish Stream Fauna Index (DSFI) and the more recent SPEcies At Risk (SPEAR) index[5], which can be coupled to the TU in order to identify the dominant sources of toxicity.

3. Results and Discussion

In total, 32 pesticides were detected in at least one phase: 18 herbicides, 7 fungicides and 7 insecticides. In addition to hexachlorobenzene, never authorized for use as a fungicide in Denmark, another 9 compounds were detected comprising metabolites, intermediates, potential impurities or isomers of a pesticide. Results show that pesticides were major contributors to the overall ecological impairment of the studied streams. This was determined using the SPEAR index, but was not recognized by the currently-approved DSFI method. Chemical toxicity analyses identified sediment-bound insecticides such as chlorpyrifos and hexachlorobenzene as the primary source for ecotoxicity in the studied streams, even when using a safety factor to account for a decreased bioavailability of the particulate-bound contaminants.

Almost all pesticides not authorized for use in Denmark and pesticide metabolites and impurities, were detected during base-flow conditions when groundwater discharge is the most dominant source of inflow to the streams. Notably, inclusion of these compounds in the TU calculations significantly increased the overall toxicity for all sampling sites regardless of the flow scenario. Our findings, supported also by other published studies[8,9], indicate that bound-phase pesticide residues could be important for both acute and chronic exposures of the biota since they consistently harboured higher toxic potential than any of the dissolved-phase samples, despite the limitation of having only a few sediment samples in our study.

4. Conclusions

The presence of the groundwater pathway indicates that stream sampling during base-flow conditions can provide valuable information about the long-term fate of pesticides in groundwater. Both aqueous and sediment phases should be sampled to assess the ecotoxicological health of streams and rivers. Ideally, integrative approaches should be developed with monitoring strategies simultaneously involving chemical analyses, ecotoxicological tools and the study of population/community responses e.g. Connon et al.[10] in order to obtain a more holistic picture.

5. References

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